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# Chemical oxidation co-coagulation-flocculation for the flotation wastewater treatment of lead-zinc oxide ore from Lanping mine

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**Abstract:** The flotation wastewater produced by "lead preferred flotation-zinc flotation" all-open process with aids of mixed depressants and cationic-anionic collectors has a high turbidity and multitude of reagent contaminants, and fails to meet the discharge standards. This study objective is to remove fine solid particles and flotation reagents in this wastewater by chemical oxidation co-coagulation-flocculation process. Results of chemical oxidation tests indicate peroxymonosulfate (PMS) exhibits superior performance on decreasing COD, and the COD remarkably decreases to 71.8 mg·$L^{-1}$ with 100 mg·$L^{-1}$ PMS addition after 120 min. Moreover, the combined oxidation of radicals ($SO_4$•- and •OH) are responsible for degradation of flotation reagents ($Na_2S$, DCCH, xanthates and amine) in the wastewater. Results of experimental factors confirm that the turbidity of wastewater decreases significantly from 124796 to 71.4 NTU, and the yield of water reaches above 90% with combined usage of lime (500 mg·$L^{-1}$) and polyacrylamide (PAM, 50 mg·$L^{-1}$). Besides, the contents of S, P, N, Zn, Pb and Fe decrease, and meet the discharge standards. Results of zeta potential analysis suggest lime reduces the electrostatic repulsion between particles, and PAM plays a bridge link role between particles, accelerating the precipitation of suspended particle.

***Keywords:*** chemical oxidation, coagulation, flocculation, flotation wastewater, lead-zinc oxide ore

## 1. Introduction

China is the largest producer and consumer of lead and zinc metals in the world. Recently, the consumption rates of lead and zinc metals have raised remarkably with the increasing demand from the construction industry (Kashani and Rashchi, 2008; Kostović and Gligorić, 2015). Meanwhile, the development and utilization of lead-zinc oxide ore have attracted a substantial amount of attention with the fast consumption of zinc lead sulfide ores (Mehdilo et al., 2012; Sehlotho et al., 2018). Differential froth flotation is frequently used to treat these types of mixed ores which owns low grade, highly oxidized property and complex co-occurrence relationships between minerals (Moradi and Monhemius, 2011; Nooshabadi and Rao, 2016; Wei et al., 2021). Specifically, sulfide minerals are firstly floated, and then oxide minerals are enriched from the tailing. In fact, the flotation of oxidized lead and zinc minerals, particularly oxidized zinc minerals, is extreme difficulty. From previous reports (Ejtemaei et al., 2014; Bai et al., 2019; Feng et al., 2023; Li et al., 2018; Pan et al., 2022; Bai et al., 2018), sulfidation-amination flotation and sulfidation-xanthate flotation are generally employed to enrich the target minerals during the beneficiation of lead-zinc oxide ore. sulfidation-amination is capable of collecting zinc oxide minerals, whereas, this process has a poor selectivity for gangue minerals when the raw ore contains multitude of carbonated gangue and argillaceous minerals (Ejtemaei et al., 2011). More important, the fatty amines usually fail to step over the slime barrier, because the slime will cause significantly negative effects on the amine collectors' flotation (Zhao, 2021). Additionally, sulfurization–xanthate flotation has obvious merits for treatment of lead zinc oxidized ores even that contains plenty of slime. However, the

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zinc flotation recovery was still not acceptable due to the poor collecting capacity of xanthate (Wu et al., 2017). Therefore, a feasible technical process and targeted flotation reagent scheme are needed to cope with such type of lead-zinc oxide ore.

Yunnan Jinding Zinc Industry Co., LTD., locating in Lanping area has the world's fifth largest lead and zinc mineral resources (Xu et al., 2023). Whereas, the unexploited lead and zinc resources reserve reaches 39.88 million tons, and the potential economic value is up to 50 billion yuan. Thus, the effective beneficiation of low-grade oxidized lead and zinc ore from Lanping mine has attracted extensive interests in the mineral processing field. Recently, our team employed a new flow sheet consisted of "lead preferred flotation-zinc flotation", and an all-open flotation process consisted of "two-times lead rougher-one-time lead cleaner-two-times zinc rougher-one-time zinc cleaner" to beneficiate this ore with the aids of mixed depressants and cationic-anionic collectors for zinc recovery in a laboratory scale. Finally, the Pb grade in the lead rougher concentrate was 2.83%, and the Pb recovery was 57.56%. Meanwhile, the Zn grade reached 28.64% with a recovery of 83.45% (Yu et al., 2023). Although the flotation indexes are desirable, the flotation wastewater of this craft cannot meet the reuse and the discharge standards mainly due to the high concentrations of suspended solids and COD value. This was rooted from the fact that a large amount of $Na_2S$ (10000~ 14000 g/t) was used in the flotation stages of smithsonite and hemimorphite to disperse slime. Besides, high dosage of collectors (400~700 g/t xanthate) were added to reinforce the recovery of oxidized zinc minerals. Thus, the flotation wastewater has become the primary problem that restricts the development of this separation process.

Recently, the efficient treatment of mineral processing wastewater has received increased attention from researchers (Chen et al., 2009; Kang et al., 2017; Yuan et al., 2023). The conventional treatment technologies include coagulation-flocculation (Meng et al., 2018), adsorption (Amrollahi et al., 2019), biodegradation (Lin et al., 2022) and chemical oxidation (Ewen et al., 2002). Whereas, there are still many issues in the treatment of flotation wastewater by traditional methods. For example, coagulation or flocculation fails to effectively treat the mineral processing wastewater with high contents of heavy metal or flotation reagents (Lee et al., 2012); the microbial method takes a long duration to degrade organic contaminants (Lou et al., 2021). Additionally, the conventional chemical oxidation methods have an extremely low treatment efficiency, and is difficult to settle the solid suspended matter in the wastewater (Neyens and Baeyens, 2003; Meng et al., 2018). Therefore, it is vitally important to develop a union process for solving the problem of flotation wastewater pollution.

In this paper, we provide the details about the research on the application of chemical oxidation co-coagulation-flocculation to remove fine solid particles and flotation reagents in the flotation wastewater of the lead-zinc oxide ore from Lanping mine. The main goals of this study were: (1) ascertaining the quality of flotation wastewater of lead-zinc oxide ore; (2) evaluating operational conditions of chemical oxidation tests (oxidant species, dosage and oxidant time); (3) determining the main experimental factors of coagulation-flocculation tests (coagulant type, dosage and PMA dosage); (4) identifying the chemical oxidation co-coagulation-flocculation mechanism. This study may provide a strong basis for the effective treatment of similar flotation wastewater.

## 2. Materials and methods

### 2.1. Materials and reagents

The raw material was collected from an oxidized lead and zinc ore from Lanping mine in Yunnan, China. Smithsonite ($ZnCO_3$) and cerussite ($PbCO_3$) were the main valuable metallic minerals. The oxidation rates of zinc and lead was about 85% and 80% although a small amount of galena (PbS) and sphalerite (ZnS) were concomitant in the ore. Calcite ($CaCO_3$), siderite ($FeCO_3$), and quartz ($SiO_2$) were the main gangue minerals. The main chemical composition of the oxidized lead and zinc ore was shown in Table 1. The wastewater sample used in present study was obtained from the laboratory flotation tail water of a lead-zinc oxide ore beneficiation. Specifically, the Pb rougher concentrate, Zn concentrate and tailing were conducted by filtration firstly, and then the filtrates were stored and serviced as the wastewater sample (as depicted in Fig. 1). From Fig. 1, the total $Na_2S$ dosage was 14000 g/t, the anionic collector (i.e., xanthates) dosage was 650 g/t, and the dosage of cationic collector (i.e., amine) was 400 g/t. Additionally, the dosage of DCCH (an organic agent containing multiple carboxyl and hydroxyl functional groups (Yu et al., 2023) was 400 g/t. On the one hand, residual xanthate and sodium sulfide are easily combined with heavy metal ions, accelerating the migration and enrichment of heavy metal ions and further polluting water bodies. Besides, xanthate is easy to decompose and produce carbon disulfide ($CS_2$) molecules, deteriorating the ecological environment. One the other hand, the residual reagents in the flotation wastewater will decrease the COD content of water bodies, posing a serious threat to biological systems. Thus, it could be speculated that these residual flotation reagents in the tailings would cause the potential threat to the surrounding ecological environment. The flotation wastewater was collected, mixed and filtered with a 50 μm of filter paper. Then, the filtrate was set for 24 hours, and was conducted by the water quality analysis. The quality analysis results of flotation wastewater of lead-zinc oxide ore were shown in Table 2. From Table 2, the flotation wastewater exhibited a significant property with high alkali, turbidity and organic matter content. Additionally, laser diffraction technology (Mastersizer, 2000; Malvern instruments) was used to measure the PSD of suspended solids in the flotation wastewater samples (as shown in Fig. 2). The results indicated that the average particle size was about 1.1 μm, and the cumulative volume distribution occupied approximately 85.9% for the suspension particle with a size below 1.6 μm.

Lime, ferric chloride, starch and polyaluminum chloride were used as the coagulant. Polyacrylamide (PAM, ten million molecular weight) was used as the flocculant. $H_2O_2$ (non-stabilized, 30wt%), $KMnO_4$, NaClO and peroxymonosulfate (PMS, $KHSO_5 \bullet 0.5KHSO_4 \bullet 0.5K_2SO_4$) were served as the oxidizing agent. Additionally, HCl and NaOH was used as the pH regulator. The present reagents were of analytical grades and purchased from different domestic chemical reagent companies.

Table 1. Main chemical composition of lead-zinc oxide ore (mass fraction, %)

| **Element** | Pb | Zn | $K_2O$ | Au* | Cu |
|---|---|---|---|---|---|
| **Content** | 0.84 | 7.4 | 0.81 | 0.06 | 0.009 |
| **Element** | Fe | As | CaO | MgO | $SiO_2$ |
| **Content** | 5.37 | 0.042 | 26.02 | 0.79 | 18.96 |

* Unit g/t

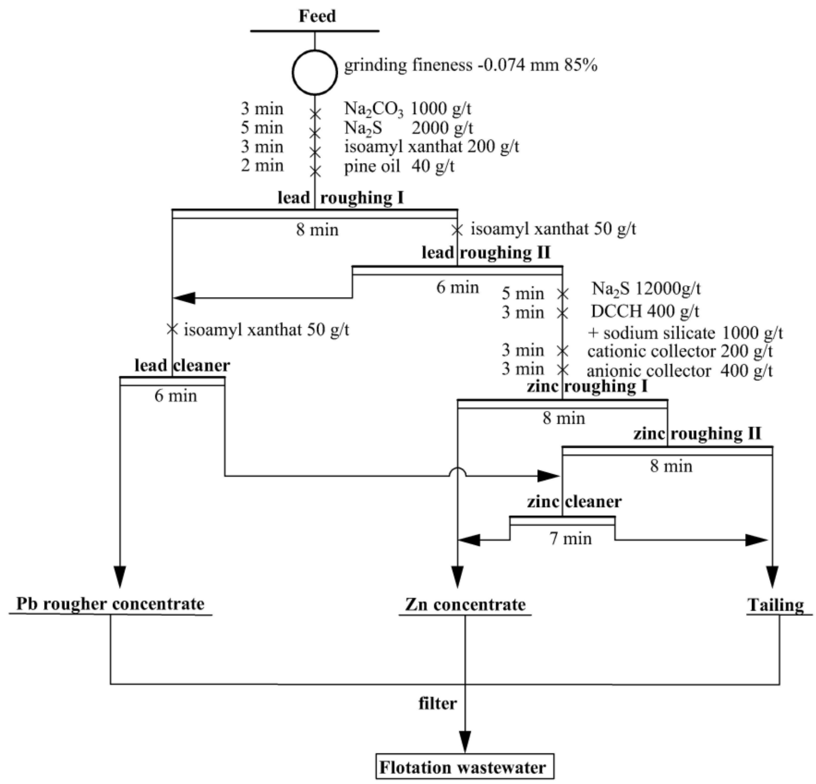


Fig. 1. The flotation flowchart of the lead-zinc oxide and the flotation wastewater samples

Table 2. Quality analysis results of flotation wastewater of lead-zinc oxide ore

| Water quality index | Appearance | Suspended solids/ mg·L$^{-1}$ | Turbidity /NTU | COD /mg·L$^{-1}$ | S /mg·L$^{-1}$ | TP /mg·L$^{-1}$ | TN /mg·L$^{-1}$ | Zn /mg·L$^{-1}$ | Pb /mg·L$^{-1}$ | Fe /mg·L$^{-1}$ | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Flotation wastewater | claybank | 2147 | 124796 | 2158.4 | 346.7 | 1.45 | 5.36 | 2.81 | <0.07 | 2.25 | 10.8 |

* COD: Chemical oxygen demand. * TP: Total phosphorus. * TN: Total nitrogen.

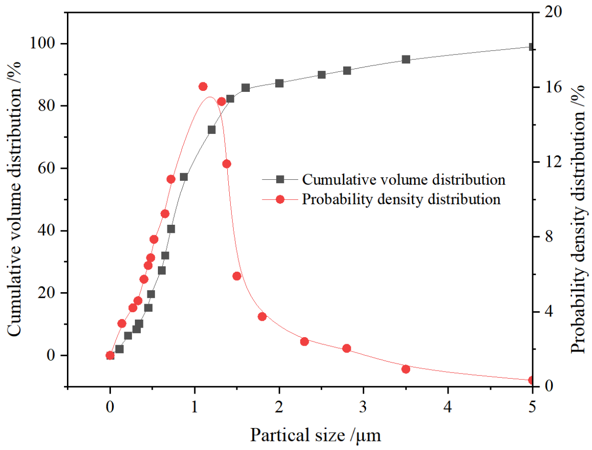


Fig. 2. Results of suspension particle size in the flotation wastewater samples

## 2.2. Experiment procedures

### 2.2.1. Chemical oxidation experiments

50 mL of initial flotation wastewater solutions were placed in a beaker, then diluted HCl solutions were added to adjust the solution pH at 9. Following, a certain amount of oxidizing agent was added to the solution with continuous mechanical stirring at 300 rpm for 90 min at a room temperature of 25 ◦C. Finally, 3 mL samples were taken out and conducted by the COD analysis. For the experiments of effects of oxidant time on the COD of wastewater, 80 mg·L$^{-1}$ PMS was added to the solution (after pH regulation at 9) with continuous mechanical stirring at 300 rpm. After a certain interval of reaction, 3 mL samples were taken out and conducted by the COD analysis.

### 2.2.2. Coagulation-flocculation experiments

500 mL of homogeneous flotation wastewater solutions were placed in a beaker, then a certain amount of coagulants and flocculant were added into the solution in turn with continuous mechanical stirring according to the presupposed speed and time. Then, the turbidities of samples were detected. Meanwhile, yield of water that was calculated by Eq (1) was used to assess the coagulation-flocculation effectiveness.

$$\eta = \frac{m_1}{m_2} \times 100\% \tag{1}$$

where $\eta$ (%) represented yield of water; $m_1$ (g) was the wastewater mass after the treatments of PMS, lime and PAM, and $m_0$ (g) was the flotation wastewater mass after the treatment of PMS.

### 2.2.3. Zeta potential measurements

Zeta probe analyzer (Zetasizer-3000HS, Malvern Instrument, UK) was selected to measure the zeta potentials of flotation wastewater under different treatment conditions. Then, 30 mL initial flotation wastewater and 20 mL of electrolyte solution (0.01 mol/L KCl) were used to prepare the suspension solution. The solution was adjusted with HCl and NaOH to a target pH value. Then, specific reagents (500 g/t lime and 50 mg·L$^{-1}$ PAM) were added and stirred for 3 min. After 5 min of setting suspension, zeta potentials of the samples were measured artificially. Besides, the zeta potential measurements of blank sample without the addition of lime and PAM were performed as control trials. Three replications of Zeta potential measurements were performed to provide arithmetic mean and error bars.

#### 2.2.4. Identification and analysis of active radicals

50 mL of initial flotation wastewater solutions were placed in a beaker, then diluted HCl solutions were added to adjust the initial solution pH at 9. Following, 80 mg·L$^{-1}$ of PMS was added into the solution with continuous mechanical stirring at 300 rpm for 5 min. Then, EPR test was performed using DMPO as a trapping agent to detect the active radicals.

## 3. Results and discussion

### 3.1. Chemical oxidation tests

#### 3.1.1. Effects of oxidant species and dosage on the COD of flotation wastewater

$H_2O_2$, $KMnO_4$, NaClO and PMS were served as the oxidizing agent to decrease the COD of flotation wastewater, and the results were shown in Fig. 3 (conditions: the solution pH was 9 and the stirring rate was 300 rpm with 90 min). As shown in Fig. 3(a), $H_2O_2$ and $KMnO_4$ presented a similar rule on the COD lower, and the $KMnO_4$ exhibited more superior performance on decreasing the COD of flotation wastewater than that of $H_2O_2$. Specifically, the COD decreased from 1024.3 to 79.5 mg·L$^{-1}$ when the dosage of $KMnO_4$ increased from 100 to 600 mg·L$^{-1}$. It is well accepted that the oxidizing ability of $KMnO_4$ is stronger than that of $H_2O_2$, and the $KMnO_4$ therefore displays preferable degradation efficiency of chemical contaminants in the solution (Wei et al., 2019). It could be inferred from Fig. 3(b) that PMS was more efficient in decreasing the COD of flotation wastewater than that of NaClO. Specifically, the COD decreased from 814.5 to 82.5 mg·L$^{-1}$ when the dosage of PMS increased from 20 to 120 mg·L$^{-1}$. PMS was the best candidate oxidizer in present study due to its strong oxidizing ability and relatively low dosage. Moreover, the usage of PMS could avoid the impurities to sneak into the solution system. Therefore, the recommended dosage of PMS was 100 mg·L$^{-1}$, and the COD of flotation wastewater was 82.5 mg·L$^{-1}$.

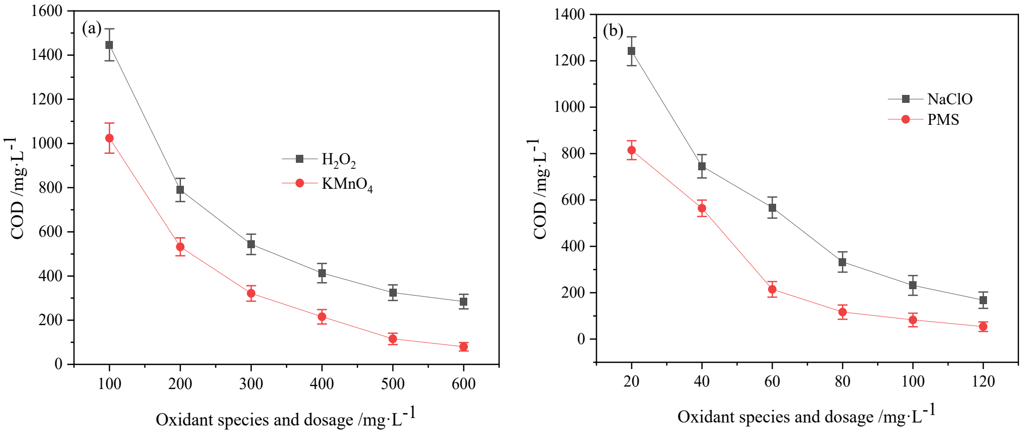


Fig. 3. Effects of oxidant species and dosage on the COD of flotation wastewater

#### 3.1.2. Effects of oxidant time on the COD of flotation wastewater

Effects of oxidant time on the COD of flotation wastewater was investigated, and the results were shown in Fig.4. The experimental conditions were as follows: the solution pH was 9, PMS dosage was 100 mg·L$^{-1}$, and the stirring rate was 300 rpm. From Fig.4, the COD of flotation wastewater decreased from 214.5 to 71.8 mg·L$^{-1}$ with the increase of oxidant time from 30 to 120 min. A further increase in oxidant time, feeble changes in the COD were observed. This phenomenon mainly attributed the combined oxidation of radicals (such as $SO_4{\bullet}^-$ and $\bullet OH$) produced by PMS decomposition (Wang and Dong, 2023). Thus, the recommended oxidant time was selected as 120 min. Given these results, PMS exhibited desirable oxidation efficiency to realize the degradation of chemical contaminants in the wastewater effectively.

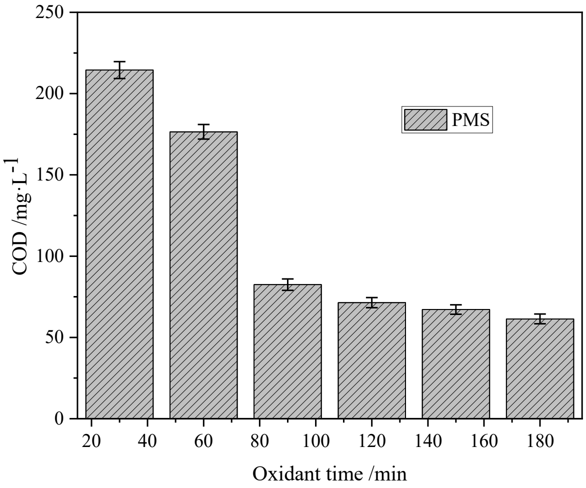


Fig. 4. Effects of oxidant time on the COD of flotation wastewater.

## 3.2. Coagulation-flocculation tests

### 3.2.1. Effects of coagulant type and dosage on flotation wastewater quality indexes

Different kinds of coagulants were added to the flotation wastewater system once treated by PMS chemical oxidation to accelerate the sedimentation of suspended particles as the natural sedimentation method failed to remove the suspended particles from the wastewater ideally (as indicated by Table 1). Effects of coagulant type and dosage on flotation wastewater quality index were investigated in details. As shown in Fig.5, the addition of coagulants facilitated the sedimentation of suspended particles. The influence order of turbidity lower of wastewater was as follows: lime＞starch＞polyaluminum chloride ＞ferric chloride [Fig.5 (a)]. Meanwhile, the influence order of yield of water was: lime＞starch＞ferric chloride＞polyaluminum chloride [Fig.5 (b)]. Thus, lime displayed a superior performance on improvement of wastewater quality indexes. When the lime dosage increased from 100 to 500 mg·$L^{-1}$, the turbidity of wastewater decreased from 1242 to 225 NTU. Meanwhile, the yield of water increased from 62.4% to 82.4%. A further increase in the lime dosage to 1100 mg·$L^{-1}$, the flotation wastewater quality indexes changed feebly. Obviously, the single lime coagulant failed to realize the flotation wastewater quality to meet the discharge standards (turbidity<100 NTU, GB 25466-2010) even under a high lime dosage addition. It was possible that the micro-particles presented strongly electronegative surfaces, triggering off intensive repulsion between particles. Accordingly, a lime dosage of 500 mg·$L^{-1}$ was selected for subsequent experiments considering the cost-effectiveness.

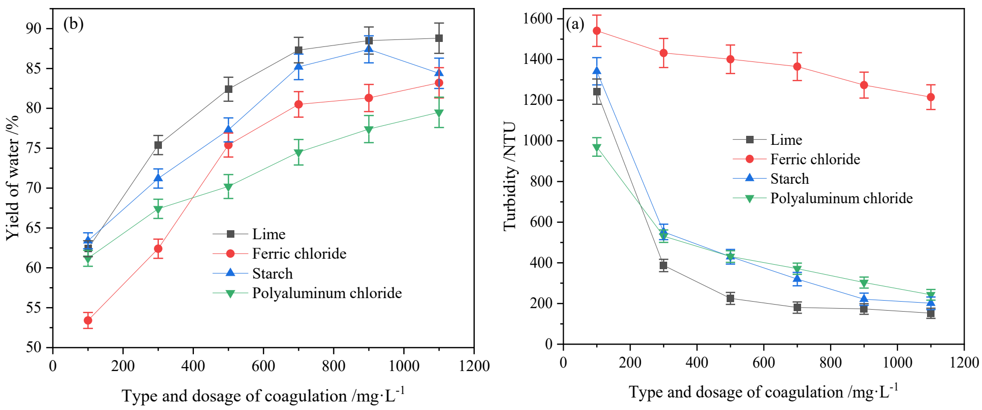


Fig. 5. Effects of coagulant type and dosage on wastewater quality indexes

### 3.2.2. Effects of PAM dosage on flotation wastewater quality indexes

To further improve the flotation wastewater quality indexes, PAM flocculation was added after the addition of 500 mg·$L^{-1}$ lime, and the effects of PAM dosage on flotation wastewater quality indexes were shown in Fig.6. As can been seen, the turbidity of wastewater decreased significantly from 185.8 to 85.3 NTU when the PAM dosage increased from 10 to 50 mg·$L^{-1}$. However, the flotation wastewater quality indexes changed inconspicuously when PAM dosage further increased to 60 mg·$L^{-1}$. Additionally, the yield of water reached above 90% in the presence of PAM. The results indicated that the combined usage of lime and PAM could effectively reinforce the sedimentation of suspended particles in the wastewater. This phenomenon mainly attributed to the bridging action of PAM that owns long chain and branch structure. PAM could adsorb multiple fine particles, increase the apparent particle size, and accelerate the sedimentation of suspended particles (Zeng et al., 2007). Thus, 50 mg·$L^{-1}$ of PAM was selected as the optimum dosage.

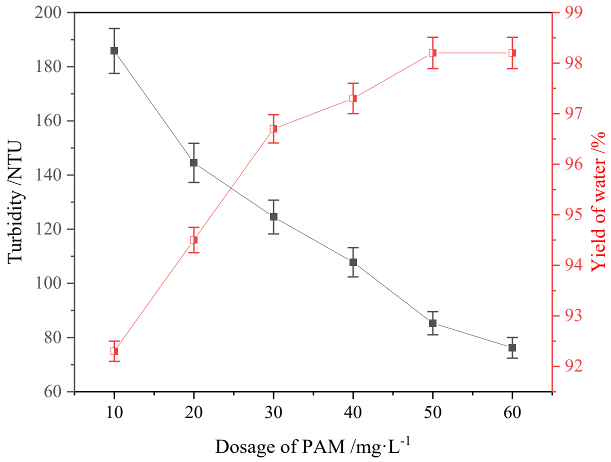


Fig. 6. Effects of PAM dosage on flotation wastewater quality indexes

### 3.2.3. Multifactor orthogonal tests

Multifactor orthogonal tests were conducted to investigate the effects of main experimental factors (lime dosage, PAM dosage, stirring time and stirring rate) on the effluent turbidity of flotation wastewater during the coagulation-flocculation processing. As shown in Table 3, the effluent turbidity of flotation wastewater decreased considerably after the treatments of coagulation-flocculation. The multifactor orthogonal tests results confirmed that the influence order of experimental factors was: lime＞PAM dosage＞stirring rate＞stirring time. Obviously, the lime played an important role in coagulation particles via neutralizing the electronegative surfaces of suspended particles, and decreasing the intensive repulsion between particles. While, the PAM could effectively accelerate the sedimentation of suspended particles. The underlying mechanism will be discussed in the following section. It was worth noting that a high strength stirring might destroy the stability of the flocs, and decrease the coagulation-flocculation effectiveness. Thus, an appropriate dosage of lime and PAM, as well as a moderate stirring rate and stirring time were essential to acquire the best treatment effectiveness.

Table 4 showed the quality analysis results of flotation wastewater after treatments of chemical oxidation co-coagulation-flocculation under the recommended conditions. From Table 4, the appearance of flotation wastewater became colorless with a pH of 8.6. The suspended solids content and turbidity were 46.5 mg·$L^{-1}$, and 85.3 NTU, respectively. Moreover, the contents of COD, S, P, N, Zn, Pb and Fe decreased remarkably comparing with corresponding results of initial wastewater (as depicted in Table 2). Herein, the chemical oxidation co-coagulation-flocculation could effectively remove fine solid particles, flotation reagents and heavy metal ions, which provided an easy access to the treatment of present wastewater.

## 3.3. Chemical oxidation co-coagulation-flocculation mechanism

### 3.3.1. Identification and analysis of active radicals

The ESR experiment was used to directly detect the generation of reactive radicals in the PMS system. As presented in Fig. 7, both DMPO-OH and DMPO-$SO_4$- adducts were observed in the PMS solution system. Moreover, the signal intensity of the DMPO-$SO_4^{\bullet -}$ adduct was much stronger than that of the

DMPO-•OH. As we known that the conversion of DMPO-$SO_4$•$^-$ to DMPO-•OH will occur inevitably as the reaction progress (Li et al., 2023). The result indicated that DMPO-$SO_4$•$^-$ was the primary active radical and the production of DMPO-•OH was insignificant in the initiation of reaction.

Table 3. Multifactor orthogonal test results

| Experimental factor | 1-Lime dosage /mg·L$^{-1}$ | 2-PAM dosage /mg·L$^{-1}$ | 3-Stirring time /min | 4-Stirring rate / r·min$^{-1}$ | Effluent turbidity /NTU |
|---|---|---|---|---|---|
| 1 | 400 | 50 | 15 | 100 | 158.50 |
| 2 | 400 | 40 | 12 | 150 | 179.30 |
| 3 | 400 | 30 | 9 | 300 | 225.8 |
| 4 | 500 | 50 | 12 | 300 | 71..40 |
| 5 | 500 | 40 | 9 | 100 | 101.50 |
| 6 | 500 | 30 | 15 | 150 | 126.8 |
| 7 | 600 | 50 | 9 | 150 | 32.40 |
| 8 | 600 | 40 | 15 | 300 | 47.80 |
| 9 | 600 | 30 | 12 | 100 | 57.40 |
| K1 | 187.87 | 87.43 | 111.03 | 115.00 | |
| K2 | 99.90 | 109.53 | 102.70 | 112.83 | |
| K3 | 45.87 | 136.67 | 119.90 | 105.80 | |
| R | 142.00 | 49.24 | 8.33 | 9.20 | |

Table 4. Quality analysis results of flotation wastewater after treatments of chemical oxidation co-coagulation-flocculation

| Water quality index | Appearance | Suspended solids /mg·L$^{-1}$ | Turbidity /NTU | COD /mg·L$^{-1}$ | S /mg·L$^{-1}$ | TP /mg·L$^{-1}$ | TN /mg·L$^{-1}$ | Zn /mg·L$^{-1}$ | Pb /mg·L$^{-1}$ | Fe /mg·L$^{-1}$ | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Flotation wastewater | Colorless | 46.5 | 85.3 | 71.4 | 0.256 | 0.21 | 1.10 | 0.015 | <0.07 | 0.12 | 8.6 |

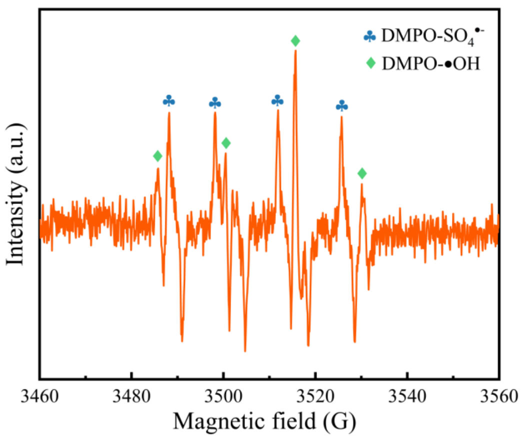


Fig. 7. ESR spectra of the reactive radicals in the PMS system

It is well known that PMS ($HSO_5^-$, pKa=9.4) is a kind of acid oxidizer with standard reduction potential. The transition metal (M) can activate the PMS decomposition, and radicals (such as $SO_4$•$^-$ and •OH) will be produced when the peroxide bond (-O-O-) accepts an electron from the transition metal (Oh et al., 2016). Thus, the presence of ions in the initial flotation wastewater might catalyze PMS decomposition as presented in Eqs. (2)-(3), forming $SO_4$•$^-$ and •OH (Xiao et al., 2019). These reactive radicals would attack the functional groups such as hydroxyl groups, carboxyl groups, amino groups, ethers groups of chemical pollutants via hydrogen capture, addition and direct electron transfer (Song et al., 2017). Ultimately, chemical pollutants ($Na_2S$, DCCH, xanthates and amine) in present flotation wastewater were degraded to smaller products such as $SO_4^{2-}$, $CO_2$ and $H_2O$, and the COD in the wastewater decreased significantly.

$$Fe(II) + HSO_5^- \rightarrow Fe(III) + SO_4^{*-} + OH^- \quad (2)$$

$$Fe(II) + HSO_5^- \rightarrow Fe(III) + SO_4^{2-} + *OH^- \quad (3)$$

### 3.3.2. Zeta potential measurements

Fig. 8 showed the zeta potential of flotation wastewater with different reagents treatments at the pH range of 3~13. As depicted in Fig.8, the initial pH value of flotation wastewater was 10.8, and the zeta potential of wastewater was about -34.4 mV. This result indicated the surface of suspended solids in the initial wastewater presented a high electronegativity, and would occur a high electrostatic repulsion force between particles, prompting the particle to disperse in the wastewater. This well explained the fact that the flotation wastewater was difficult to clear after 24 hours of natural settlement. It could be speculated the electrostatic repulsion exceeded the natural sedimentation energy, and the initial wastewater system had a high stability. When 500 mg·L$^{-1}$ of lime was added, the zeta potentials of wastewater increased rapidly during the pH range of 3~7, and then trended to decrease with a further increase of pH values. The addition of lime effectively neutralized the negative charge of solid particles surfaces, promoting the particle sedimentation. This stemmed from the fact that $Ca^{2+}$ and $Ca(OH)^+$ ions originated from lime compressed double electric layers on surfaces of suspended solid particles, and adsorbed onto the surfaces. This activity reduced electrostatic repulsion between particles. Moreover, characteristic adsorption would occur between $Ca(OH)_2$ complexes and suspended particles, increasing particle size and accelerating sedimentation of particles (Zhan et al., 2021). The related chemical reactions involved were as follows:

$$Ca^{2+} + OH^- = Ca(OH)^+ \quad (4)$$

$$Ca^{2+} + 2OH^- = Ca(OH)_2 \quad (5)$$

When lime and PAM were added, the zeta potential of wastewater presented downward trend generally comparing with corresponding results without addition of reagents. It was possible that PMA that owned the long chain and branch structure could effectively adsorb onto particles surfaces once coagulated by lime. This adsorption inevitably decreased the zeta potentials of suspended particles because PAM presented electronegativity. Additionally, PAM could play a bridge link role between particles, making fine particles to form large floc, and facilitating the precipitation of suspended particles. Thus, the finding well indicated the underlying mechanism on co-coagulation-flocculation in the presence of lime and PMA.

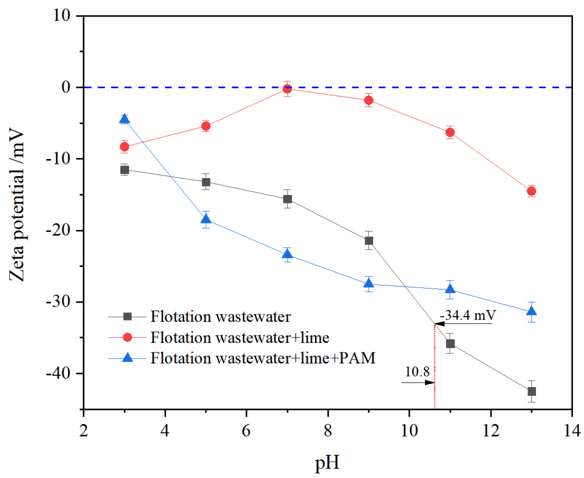


Fig. 8. Zeta potentials of flotation wastewater with different reagents treatments

## 4. Conclusions

Peroxymonosulfate (PMS) exhibited superior performance on decreasing the COD of flotation wastewater, and the COD remarkably decreased to 71.8 mg·L$^{-1}$ with 100 mg·L$^{-1}$ PMS addition after 120 min. Results of EPR demonstrated that the combined oxidation of reactive radicals (such $SO_4$•- and •OH) were responsible for degradation of flotation reagents ($Na_2S$, DCCH, xanthates and amine) in present wastewater system. The results of experimental factors confirmed that the turbidity of wastewater decreased significantly from 124796 to 85.3 NTU, and the yield of water reached above 90% with combined usage of lime (500 mg·$L^{-1}$) and polyacrylamide (PAM, 50 mg·$L^{-1}$). Besides, the contents of COD, S, P, N, Zn, Pb and Fe decreased significantly. This wastewater after treatments met the industrial wastewater discharge standards. The results of zeta potential analysis suggested lime reduced the electrostatic repulsion between particles, and PAM played a bridge link role between particles, accelerating the precipitation of suspended particles. Thus, the chemical oxidation co-coagulation-flocculation could effectively remove fine solid particles, flotation reagents and heavy metal ions, which provided an easy access to the treatment of similar wastewater.

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